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In-Situ Versus Post-Synthetic Stabilization of Metal Oxide Nanoparticles

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1. Introduction

Within the last two decades, the synthesis and application of nanoparticles has evolved as one of the most active fields of research and development, promising solutions to some of humanity's most pressing needs in cases as diverse as cancer therapy, water purification, or energy storage (Duget et al., 2006; Bazito & Torresi, 2006; Centi & Perathoner, 2009; Feldmann & Goesmann, 2010; Goyal et al., 2011; Kim & van der Bruggen, 2010; Li et al., 2008; Moghimi et al., 2005; Prandeeep & Anshup, 2009; Sanvicens & Pilar, 2008; Sides et al., 2002; Theron et al., 2007). Today, nanoparticles are predominantly being applied as particulate materials with enhanced properties as compared to the standard bulk material. One however envisions nanotechnology already in the near future to strongly increase in complexity, leading to the development of hierarchical nanosystems being capable of computing and robotic or even self-replicating tasks (Mallouk & Sen, 2009; Rasmussen et al., 2003; Requicha, 2003; Sánchez & Pumera, 2009). Most future applications are expected to be eventually realised via the so-called bottom-up approach, emanating from nanoparticles as tiny building blocks that self-assemble in a controlled and organised manner to a higher level of hierarchy (Shenhar & Rotello, 2003; Dong et al., 2007). The primary prerequisite for the realisation of this strategy is the availability of high-quality nanoparticles that can act as such building blocks, possessing a predefined and uniform size and shape. Consequently, research on the controlled preparation of nanoparticles has greatly intensified within the last two decades, mainly focusing on carbon-based nanostructures (Mostofizadeh et al., 2011), metals (Cushing et al., 2004; Guo & Wang, 2011), metal oxides (Cushing et al., 2004; Chen & Mao, 2007; Pinna & Niederberger, 2008), semiconductor nanostructures (Trindade et al., 2001) and organic or hybrid nanostructures (Biswas & Ray, 2001; Ballauff, 2003). Remarkable progress has been made in the synthesis of nanoparticles with defined and even complex shape for certain materials (Jun et al., 2006), although a general understanding of the formation processes of nanostructured materials appears to remain a long way off.

An aspect that however is often not treated accordingly is the second step in the fabrication chain: the control of the surface interactions of the nanoparticles to determine their secondary structure. Even though by now a large number of examples have been reported on the preparation of highly ordered superstructures for diverse nanoparticle systems (Gao & Tang, 2011), the truly rational and controlled self-assembly, which would be vital for the large-scale feasibility of many of the envisioned applications, appears still to be long out of

reach. Even the first level, the control of the interaction forces between the individual nanosized building blocks to avoid uncontrolled agglomeration, is neither realised nor understood in most commercial nanotechnology products today, and one is only beginning to develop general concepts aimed to describe the interactions between ultra-small particles in the low nanometer regime, even though the models of particle interaction for larger particles have been established in colloid science almost a century ago. One concept that is particularly promising for the control of nanoparticle interaction is the use of small organic ligands – in contrast to the classical models of purely electrostatic stabilisation on the one hand and polymer-based steric stabilisation on the other hand – which in principle allows long-term stabilisation with minimum stabiliser content. This Chapter is aimed to introduce the advantages and challenges of the small molecule-based stabilisation, and will present a number of select examples for the successful application of this strategy. A special focus is set on comparing the different options of introducing the stabiliser into the system: on the one hand, the so-called in-situ stabilisation strategy, where ligands are already introduced into the system prior to or during particle formation, and on the other hand the post-synthetic stabilisation, where the ligands are added in a separate step following the synthesis, in order to give the reader significant insight into this field to allow individual judgement on the benefits and disadvantages of each strategy. The Chapter will be concluded with an outlook to current and possible future developments in the field of the small-molecule stabilisation of nanoparticles.

2. The stabilisation of nanoparticles

The systematic study of the interactions between small particles began in the first decades of the 20th century within the rapidly growing field of colloids science, following the discovery that colloidal systems consist of small units below 500 nm in size dispersed in a liquid medium. In the pioneering works of Ostwald, the inherent thermodynamic instability of such colloidal systems was recognised (Ostwald, 1915), which causes a general tendency of such systems to agglomerate and aggregate, in order to minimise the particle-fluid interface area and thus the interface free energy. A number of theories were proposed in the following decades to explain the stability of colloidal systems (Everett, 1988), providing different possibilities to change and enhance the stability, which shall be briefly summarised in the following.

2.1 Colloidal theories of particle stabilisation and their application to nanoparticles

A few decades after Graham and Ostwald, first theories to explain the stability of aqueous colloidal systems in the presence of charged species were formulated, leading to the well-known DLVO theory (Derjaguin & Landau, 1941; Verwey & Overbeek, 1948). This theory is based on previous works by Hamaker on the attractive interactions of colloidal particles, which he explained as the combined van-der-Waals attractions of the individual atoms (Hamaker, 1937). These attractive forces are balanced by the electrostatic repulsion of likely charged particles, with charges not only arising from the surface potential of the particles, but also the electrochemical double layer surrounding them. Also the Born repulsion, effective only at small distances when the electron shells of atoms start to penetrate each other, is taken into account. The DLVO theory shows that the stabilisation of particles can be easily achieved by electrostatic repulsive forces, which however are highly labile and

depend on conditions such as the pH and ionic strength in the dispersion medium. Moreover, this mechanism cannot be applied to hydrophobic systems that often are preferred for the handling and manipulation of nanostructured materials, e.g. due to their lower surface tension and lower adsorption tendency to the nanoparticle surface.

Another possibility is the stabilisation by coverage of the particle surface with organic polymers. This steric stabilisation concept was investigated theoretically already briefly after the DLVO theory (Mackor, 1951). The polymer chains adsorb to the particle surface to create an organic shell around the particle. As two particles approach each other, their organic shells touch and eventually interpenetrate. At that point, the solvation shell of the polymer is disrupted, as the polymer density increases upon penetration, which creates a counteracting osmotic pressure of the solvent that forces the particles apart (Napper, 1983). Good solvent compatibility of the polymer is therefore required for an effective steric stabilisation. The electrosteric stabilisation concept involves the use of polyelectrolytes, i.e. polymers with charged groups, to attach to the particle surface, thereby combining the electrostatic and steric stabilisation concepts (Hunter, 2001).

These classic colloidal theories have been proven successful for the description of colloidal systems in numerous cases and hence, also their application to nanoparticle dispersions seems obvious. The DLVO theory has thus been applied in a number of cases to describe the behaviour of nanoparticulate systems (Schwarz & Safran, 2000; Tadmor & Klein, 2001; Reindl & Peukert, 2008; Marczak et al., 2009; Segets et al., 2011). However, some special aspects need to be taken into account when attempting to describe dispersions of nanoparticles below 20 nm in size by means of DLVO theory: On the one hand, the distance dependence of the attractive and repulsive forces is strongly dependent on particle size already in the classical DLVO concept (Verwey & Overbeek, 1948). The electrostatic interaction is simplified in colloidal models as the interaction between two planar electrochemical double layers, because the interparticle distance becomes much smaller than the particle size as the particles approach each other. For small nanoparticles, this model is no longer valid, and thus spherical double layers must be included in the calculation (Mulvaney, 1998). The interaction of small nanoparticles was studied by Wiese and Healy in 1969. They reported two significant effects when reducing the particle size to the low nanometre regime: on the one hand, the repulsive forces become very small, but on the other hand also the energy minimum becomes very shallow (Wiese & Healy, 1969). The application of the DLVO concept to such small particles generally leads to interaction potentials of only a few kT , which results in only small changes between a stable and an unstable system, making the prediction of the stability of a system a challenging task (Marczak et al., 2009; Segets et al., 2011). Moreover, the minimum is also shifted in position towards smaller interparticle distances and thus, the description of the particles as solid, spherical systems with defined interface becomes inappropriate. A molecular layer of organics adsorbed to the particle surface that may be neglected for large particles can become important for the stability of nanoparticle systems, as it may be sufficient to prevent the particles from reaching the critical distance. Additionally, inhomogeneities within the particles, such as an oxide shell of metal nanoparticles, can suddenly play an important role.

This is nicely exemplified in the work of Reindl and Peukert, who investigated the stabilisation of silicon nanoparticles in organic solvents, taking into account an oxidised silica shell around the particles as well as the adsorption of solvent molecules, by applying a

core-shell-adsorbate model based on the DLVO theory (Reindl & Peukert, 2008). Figure 1 shows the used models as well as results of the calculation of the total energy barrier. Whilst at higher concentrations, the system would be unstable for pure Si nanoparticles, the oxide shell provides high stability against agglomeration. Moreover, it is clearly visible that the adsorbate layer formed by solvent adsorption also has a noticeable effect on the energy barrier despite the relatively large particle size of 100 nm, further increasing the stability of the system. Such core-shell models have been applied also to other systems in the meantime (Marczak et al., 2009; Segets et al., 2011).

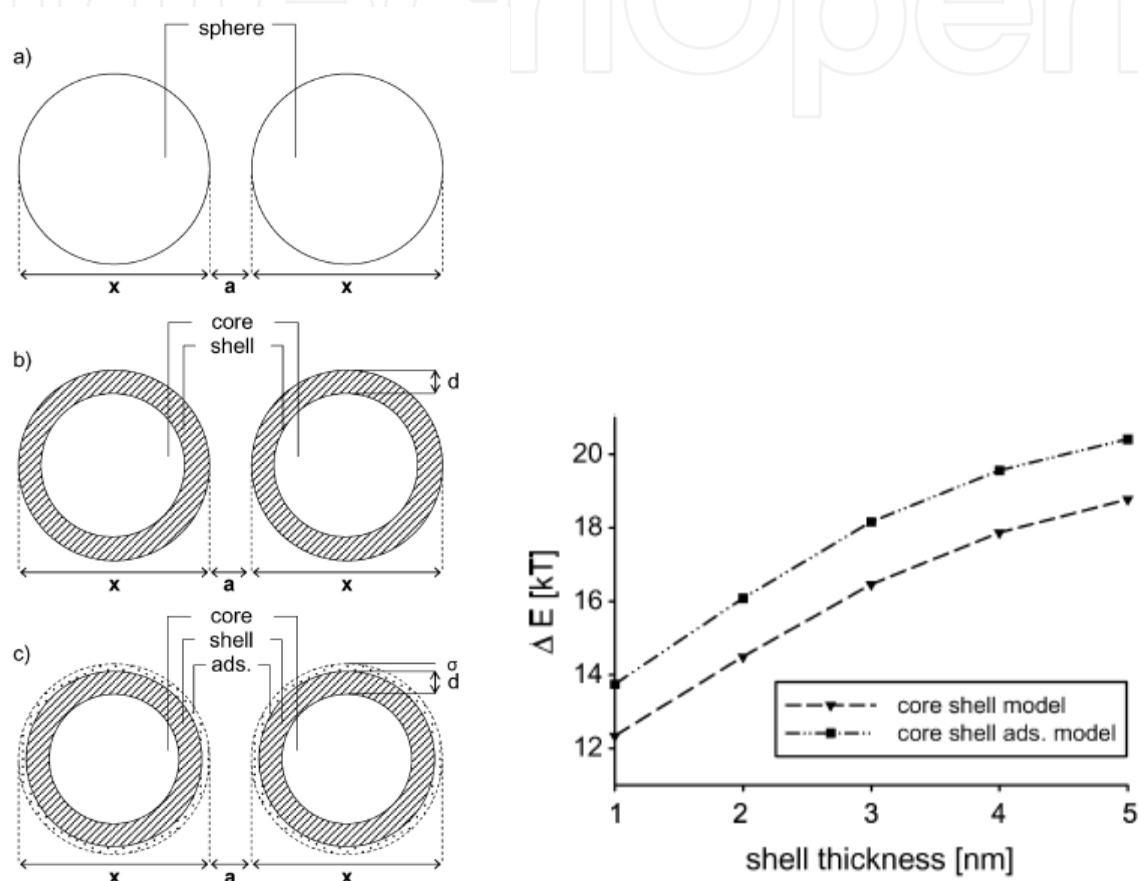


Fig. 1. Left: schematic of the model systems used for DLVO calculations on Si nanoparticles: (a) solid sphere model, (b) core-shell model, (c) core-shell-adsorbate model; right: calculated energy barrier ΔE of Si nanoparticles for the model systems in dependence of shell thickness; reproduced from (Reindl & Peukert, 2008) with kind permission of Elsevier.

On the other hand, an extension of the DLVO theory has been proposed, leading to the so-called XDLVO concept, in the works by van Oss et al. (van Oss et al., 1987, 2003). Here, Lewis acid-base interactions are additionally taken into account, and this model was shown to allow a more accurate prediction of the stability of dispersions of hectorite and chrysotile particles in various media (Wu et al., 1999). Also this concept has been applied to nanoparticle systems, being able to explain differences in the stability of iron oxide nanoparticle dispersions when adding fatty acids as stabilisers (Gyergyek et al., 2010).

The precise modelling of the steric stabilisation of nanoparticles, on the other hand, remains complex, which prevented widespread attempts to calculate particle stability by

adsorption of polymers. To allow a practical application, several simplified models were presented, such as the theory of Vincent and Edwards (Vincent et al., 1986). Here, a uniform polymer segment density is assumed within the polymer shell, thus requiring a smaller number of parameters. This model has also been applied to the steric stabilisation of nanoparticles. For example, K. Lu investigated the interaction energies of Al_2O_3 nanoparticles of 20–45 nm in size stabilised with polymeric shells of different thickness (Lu, 2008). Figure 2 shows the results of these calculations, clearly revealing that with increasing layer thickness, the stability of the system clearly increases, and that a critical layer thickness is required to prevent agglomeration (in this case, amounting to 2.5 nm), according to the model.

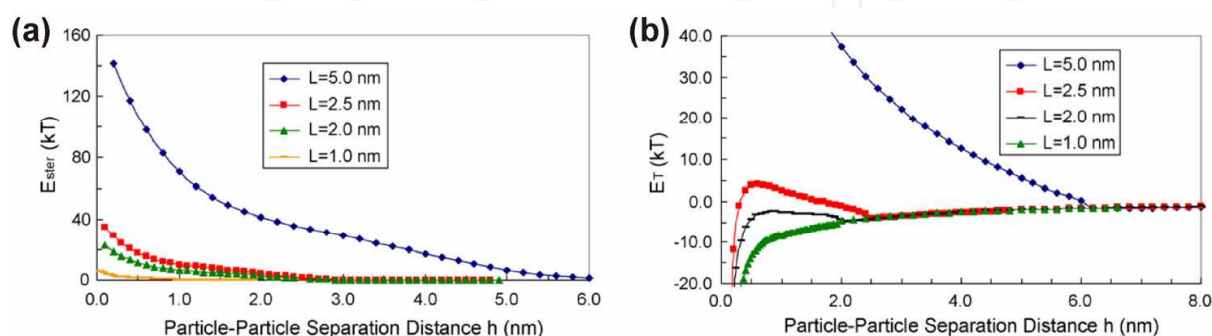


Fig. 2. Calculation of the distance-dependent steric interaction energy E_{ster} (a), and the total interaction energy E_T (b) for the stabilisation of Al_2O_3 nanoparticles protected by polymer shells of different thickness (Reproduced from (Lu, 2008) with kind permission of Elsevier).

2.2 The small-molecule stabilisation concept

Whilst the classical colloidal models of electrostatic and steric stabilisation have thus been known for decades, the treatment of nanoparticles to obtain stable dispersions in practice has always followed an empirical approach, with the well-known gold nanoparticle sols serving as typical examples that small organic molecules are sufficient to act as long-term effective stabilisers to prevent agglomeration (Turkevich et al., 1953). In many cases, the precise mechanism of stabilisation is unclear, and it is generally still being disputed whether organic ligands bound to the surface in most cases bear charges that result in electrostatic stabilisation, or whether steric repulsion effects (Peyre et al., 1997; Shah et al., 2001; Arita et al., 2009) or in fact some combined effects (Marczak et al.; 2009, Segets et al., 2011) determine the stability of the system.

Nonetheless, it has become clear that this concept of adsorption of small molecules, resulting in very thin organic layers (termed adlayers) around nanoparticles, has significant advantages over a conventional steric stabilisation with polymers: The packing of small particles is strongly influenced by the adlayer thickness Δ , basically equivalent to the chain length of the surface-bound ligands, as shown in Figure 3. For long-chain ligands, such as a polymer coating, the large adlayer thickness results in a much lower packing density of the particles as compared to short-chain ligands.

This can also be expressed as the effective volume fraction Φ_{eff} which includes the adlayer in the particle volume and is related to the true volume fraction Φ of the particles by

$$\Phi_{eff} = \Phi \left(1 + \frac{\Delta}{r} \right)^3 \quad (1)$$

r referring to the particle radius (Bell et al., 2005). Hence, the particles can be packed less densely, which limits the maximum achievable solids volume fraction in concentrated dispersions, leads to higher viscosity for a given volume fraction, and results in a “dilution” of core particle properties in applications such as nanocomposites.

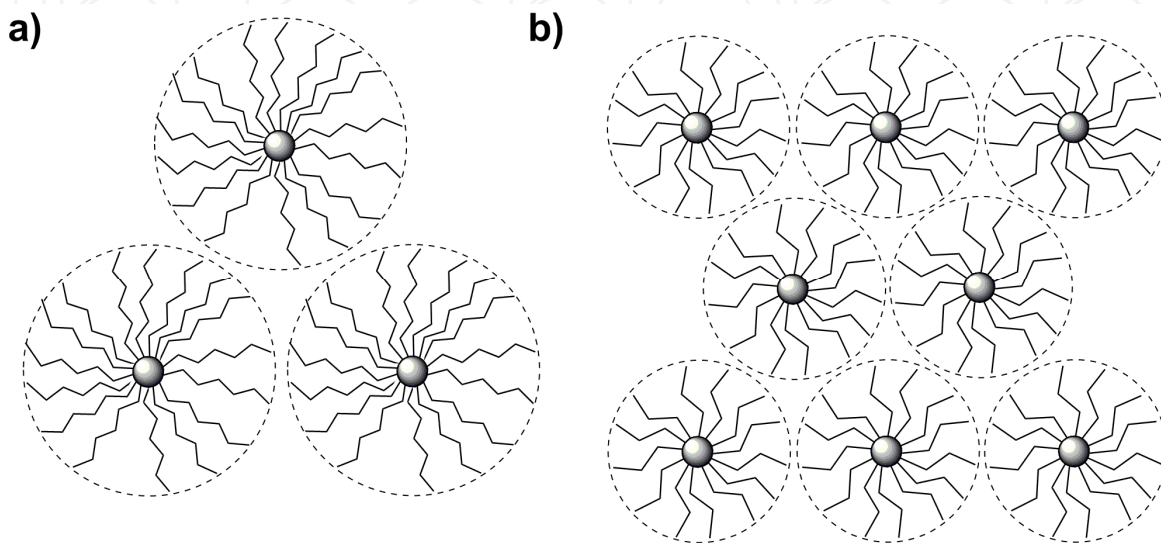


Fig. 3. Schematic (not to scale) of the packing of spherical particles with a stabilising adlayer comprised of long-chain ligands (a) and short-chain ligands (b).

3. In-situ stabilisation of nanoparticles

The stabilisation of nanoparticles can be realised experimentally most easily via the in-situ stabilisation concept. This involves the addition of stabilisers or ligands to the reaction system already during or even prior to nanoparticle formation. Hence, it is straightforward, and in principle can lead to optimum stabilisation, as it prevents particle agglomeration *a priori*, but on the other hand bears the imminent risk of an alteration of the nanoparticle formation process – an aspect that in some cases may even be desired, e.g. to obtain smaller and more uniform particles, but in many other cases is unwanted, as it makes the formation mechanism even more complex, or results in a degradation of intrinsic properties of the nanoparticles. Conceptually, the in-situ stabilisation of nanoparticles can be performed with optimised stability in the reaction medium when the processing or application of the nanoparticles in that medium is desired or feasible. In other cases, an intermediate precipitation step is performed to facilitate a change in dispersion medium, for example when a more volatile or more hydrophilic/hydrophobic medium is required than was used for the synthesis, and thus, the stabiliser is targeted to result in optimised stability in the final medium rather than the reaction solvent.

The in-situ stabilisation strategy has found widespread application, as the addition of surfactants or surface-modifying agents to a reaction mixture is commonly employed in the synthesis of metal nanoparticles (Turkevich et al., 1953; Murphy et al., 2005) as well as in the

so-called hot injection method, where the precursors are injected into a hot solvent/surfactant mixture, resulting in highly uniform and well-dispersible nanocrystals (Murray et al., 1993). This method has also been extended to transition metal oxides (Rockenberger et al., 1999; Sun et al., 2004; Epifani et al., 2008; Gilstrap Jr. et al., 2008). Despite the widespread use of in-situ stabilisation, the precise effect of the ligands on the properties of the resulting products has only been investigated in a small number of studies. Only a few studies were directed towards a systematic investigation of the effect of ligands on the particle properties, whilst in most reports the influence of the chemistry of the ligand has not been studied specifically. In the following section, some recent investigations of ligand effects on the particle properties are presented for different metal oxide nanoparticle systems.

3.1 Effects on particle crystallinity

Most ligands possess Lewis-basic groups that act as electron donors to metal centres on the nanoparticle surface, thereby enabling a firm binding of the ligands. Naturally, these groups also coordinate to molecular complexes of the same metal and hence, also to the precursor species. If the ligands are coordinated more strongly than the organics in the precursor complex, the reaction rates during the particle formation are decreased drastically, a fact that is utilised in aqueous sol-gel chemistry to deliberately decrease the rates of condensation in many cases. For strongly coordinating ligands, this may even lead to an incomplete formation, resulting in substantial organics content or a decrease in crystallinity of the resultant nanoparticles, a loss of yield, or may even impede the formation of nanoparticles altogether.

The effect of ligands on the crystallinity of in-situ stabilised titania nanoparticles has been investigated in a number of studies, because the crystallinity and phase of the particles is crucial to their performance in photocatalytic applications (Chen & Mao, 2007). Thereby, the high suitability of catechol ligands for the in-situ surface modification of TiO₂ nanoparticles, due to a very strong, covalent binding, has been reported (Niederberger et al., 2004). If a certain, critical concentration of these ligands however is exceeded and the molar Ti:ligand ratio becomes smaller than 10, a substantial decrease in crystallinity is observed (Niederberger et al., 2004). Therefore, the dopamine ligands cannot be used in high amounts, which results in the additional presence of the reaction medium benzyl alcohol on the particle surface after the synthesis (Niederberger et al., 2004). In this example, the in-situ stabilisation process did not lead to stability in benzyl alcohol but in various common organic solvents after centrifugation, washing and redispersion steps. Furthermore, different substituted catechols were investigated. Depending on the precise chemistry of the catechol side group, the particles could be made more hydrophilic or hydrophobic, even allowing stability in water when using dopamine hydrochloride as ligand (Niederberger et al., 2004).

In a more recent study, we have taken a closer look at the precise influence of the chemistry of the ligands on the crystallinity (Garnweitner et al., 2010). Different ligands with amine, alcohol and/or carboxylic acid functional groups were added prior to the synthesis of TiO₂ nanoparticles, again in benzyl alcohol as reaction medium. Interestingly, strong differences were found with respect to stability of the resulting nanoparticles, as well as their crystallinity; the differences in these properties however could not be directly correlated. Figure 4 (left) shows a series of X-ray diffraction (XRD) patterns measured from products obtained in presence of different ligands. Under the chosen experimental conditions, in the

ligand-free system small anatase nanoparticles with good crystallinity and a size of about 3 nm are obtained. Whilst for glycine and malonic acid, no negative effects on crystallinity could be observed, for malic acid and glycerol a strongly decreased crystallinity was found. This could be correlated to the binding of the ligands to the particle surface by means of thermogravimetric analysis (TGA), showing that malic acid and especially glycerol bind to the nanoparticles in substantially higher quantities than the other ligands, equivalent to a higher mass loss (Figure 4, right).

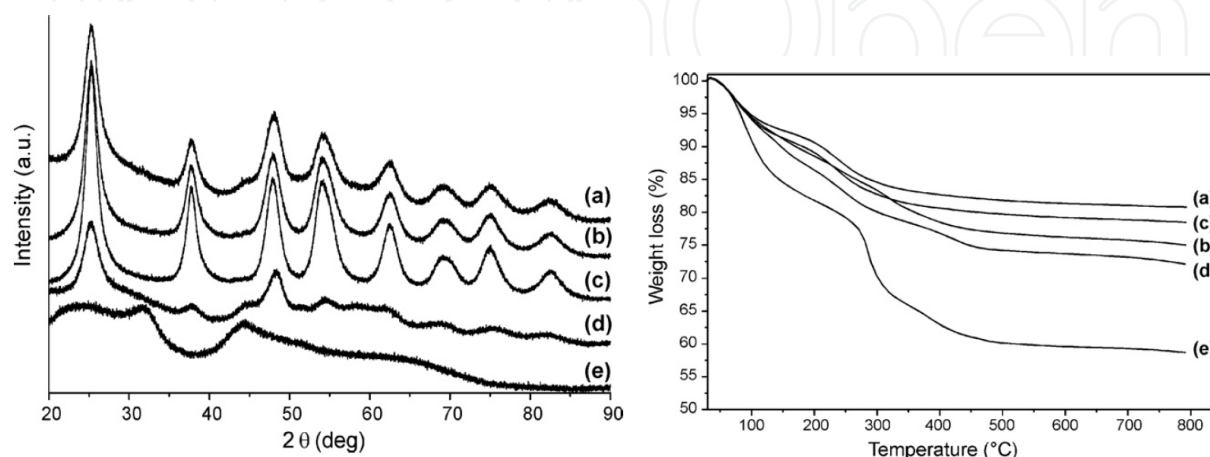


Fig. 4. X-ray diffractograms (left) and thermograms (right) of samples obtained without any present ligands (a), and in the presence of glycine (b), malonic acid (c), malic acid (d) and glycerol (e). Images reproduced from (Garnweitner et al., 2010) with kind permission of Elsevier.

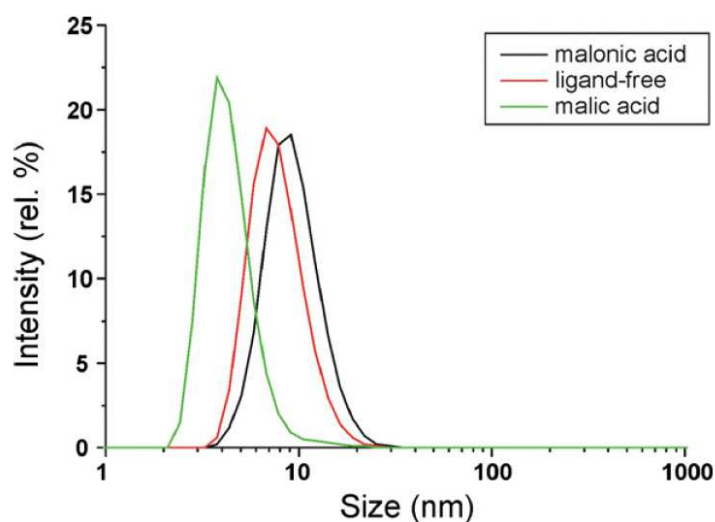


Fig. 5. Particle size distribution of TiO_2 nanoparticles modified in-situ by addition of various ligands, as determined by dynamic light scattering. Reproduced from (Garnweitner et al., 2010) with kind permission of Elsevier.

Surprisingly, the stability of dispersions of the nanoparticles could not be directly related to these results. The stability was investigated after precipitation of the particles in diethyl ether and redispersion by simple addition of de-ionised water to the precipitate. Best stability – in terms of highest solid content for minimal water addition – was observed for

the glycine and malic acid systems (Garnweitner et al., 2010). However, good stability was even achieved for the ligand-free system, as in this case, the reaction of TiCl_4 with benzyl alcohol causes the formation of HCl as byproduct, resulting in a highly positive zeta potential. The secondary particle size distribution, as determined by dynamic light scattering (DLS), did not reveal substantial differences between the samples (Figure 5), which – in combination with the TGA results – proves that the reaction medium coordinates to the particle surface in addition to any ligand, and that for most systems, the ligand merely replaces the reaction medium rather than forming an additional shell.

3.2 Effects on particle size and morphology

Although the effect of in-situ stabilisers on the morphology of metal oxide nanoparticles has been studied in a number of publications, as these stabilisers were often purposely used to modify particle size, consistent knowledge on the precise influence of the stabilisers has not been reached, probably due to the complex interaction and the necessity of a thorough analysis of the underlying chemistry to be able to understand the effects. Gaynor et al. investigated the effect of soluble hydroxypropylcellulose on the particle size of TiO_2 nanoparticles, reporting a rather complex effect (Gaynor et al., 1997). The in-situ stabilisation of magnetite nanoparticles with L-arginine was investigated by Theerdhala et al., who showed that the particle size decreased steadily with decreasing precursor:stabiliser ratio, with however rather broad size distributions and additional changes in aspect ratio of the particles (Theerdhala et al., 2010).

In other cases, the addition of ligands even in small amounts was shown to result in dramatic changes in morphology. Again, TiO_2 nanoparticles are among the best studied systems: The influence of amino acids used as in-situ ligands in a “gel-sol” synthesis of anatase nanoparticles was investigated by Kanie and Sugimoto, showing that for certain amino acids, the initial particle-type morphology changes to rod-like due to strong adsorption of the amino acids to specific crystal faces (Kanie & Sugimoto, 2004). The synthesis of TiO_2 nanorods by hydrolysis of titanium tetraisopropoxide in presence of oleic acid was investigated by Cozzoli et al., who even proposed a model to explain different morphologies obtained for a “fast” and “slow”-type hydrolysis, again involving selective adsorption of the ligand (Cozzoli et al., 2003).

As another example, Polleux et al. investigated the synthesis of tungsten oxide nanostructures in a nonaqueous system, using benzyl alcohol as reaction medium (Polleux et al., 2006). In the pristine system, comprising only the precursor and solvent, nanoplatelets of about 5-10 nm in thickness and 30-100 nm lateral size were obtained (Figure 6, a), but after addition even of small amounts of 4-*tert*-butylcatechol, anisotropic rod-like structures with diameters of 35-40 nm and lengths of 50-800 nm were observed (Figure 6, b-d), which in fact are comprised of a highly ordered lamellar organic-inorganic hybrid nanostructure (Polleux et al., 2006). The ligand was hence inferred to act in manifold ways, not only controlling the crystal growth through selective binding to high surface energy edges but also the interaction of the individual platelets to enable their assembly (Polleux et al., 2006). Although in this example, the dispersibility of the obtained nanostructures in various organic solvents was not specifically investigated, the tremendous effect of organic ligands on the morphology of inorganic nanostructures is nicely illustrated. A broader review of these effects can be found in our earlier publication (Garnweitner & Niederberger, 2008).

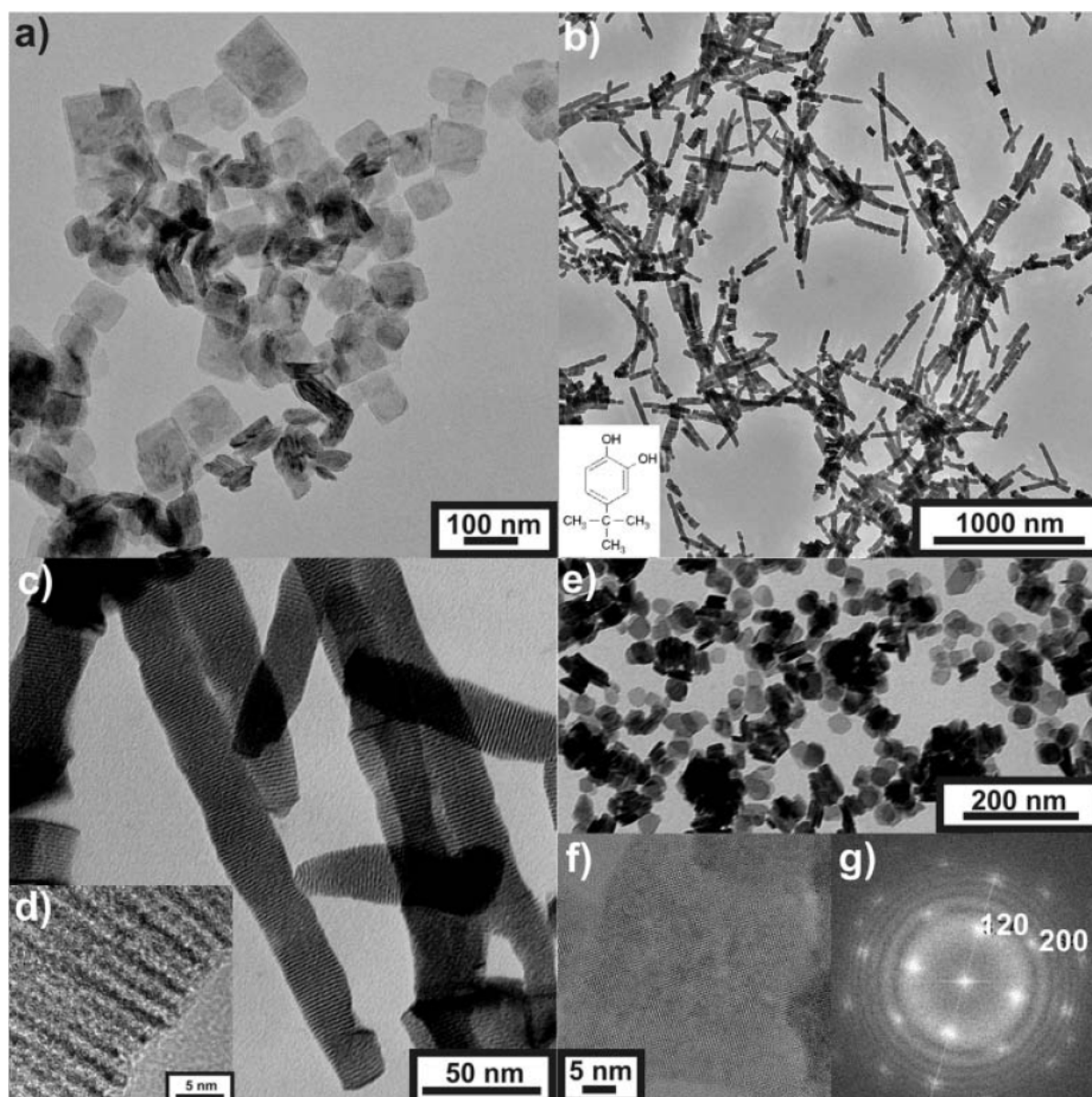


Fig. 6. TEM images of tungstite nanoparticles obtained without 4-*tert*-butylcatechol (a), and of the hybrid nanostructures obtained in the presence of 4-*tert*-butylcatechol, as-prepared (b-d) and after redispersion in water (e-g). The chemical structure of the ligand is shown in (b, Inset) (Polleux et al., 2006). Reproduced by permission of the Royal Society of Chemistry.

4. Post-synthetic stabilisation

The biggest advantage of the post-synthesis stabilisation approach is that the original synthesis is preserved, with particle properties such as size and crystallinity being unaffected by the successive stabilisation treatment that is performed at much more lenient conditions than the synthesis. Under these conditions, a possible unwanted reaction or decomposition of the stabiliser can also be excluded, thus allowing higher flexibility in terms of ligand structure and chemistry. On the other hand, after the synthesis already rather strong agglomerates may be present, and organic species from the reaction may be strongly adsorbed to the particle surface, thus limiting or preventing the stabilisation.

The post-synthetic modification of metal oxide nanoparticles has been investigated in a large number of cases, and with very different goals, not only for an enhancement of colloidal stability of the nanoparticles, but also to adjust many other properties, for example the optical and photocatalytic performance (Rehm et al., 1996; Rajh et al., 1999, 2002; Stowdam & van Veggel, 2004). Different classes of surface modifiers that have shown to be especially suitable for metal oxides include alkoxysilanes and chlorosilanes (Sanchez et al., 2001), carboxylic acids (Bourlinos et al., 2002; Arita et al., 2010), or phosphonic/phosphoric acid derivatives (Rill et al., 2007; Lomoschitz et al., 2011). Interestingly, whereas in some systems, the binding of ligands can be perceived as an exchange process of previously surface-coordinated organics (Shenhar & Rotello, 2003), in other systems a grafting of ligands to a formerly “bare” surface was observed (Arita et al., 2010). Many other groups use the term “surface modification” without further specification of the chemical surface processes. Apparently, differences between the individual systems do exist, and in contrast to the well-explored metal and semiconductor nanoparticle systems, further investigations will be required to fully understand and explain the processes during post-synthetic stabilisation of metal oxide nanostructures. Within the scope of this Chapter, only some select examples can be shown to illustrate the potentials of post-synthetic stabilisation strategies.

4.1 Exchange chemistry of metal oxide nanoparticles

The exchange chemistry of γ -Fe₂O₃ nanoparticles has been investigated in detail by Boal et al. (Boal et al., 2002). Here, alkylamine-protected maghemite nanoparticles were subjected to different tailor-made long-chain ligands (Figure 7). The amines were exchanged at least partially by all alcohol ligands used; however substantial differences in the stability of the modified particles were observed: whilst dodecanol (1)-modified nanoparticles agglomerated within a few days both when being in dispersion and in a dried state, modification of the nanoparticles with pentacosane-13-ol (2) and 13-dodecylpentacosane-13-ol (3), bearing two and three C₁₂-chains, respectively, resulted in high stability of the nanoparticles in the solid state after initial precipitation. Long-term stability in dispersion, however, was only obtained when using ligands with bidentate diol anchoring groups. Again, ligands with only a single C₁₂ chain (4) showed low stability after drying, whilst double-chain bidentate ligands (5) proved most effective, leading to long-term stability both in dispersion and in the dried state (Boal et al., 2002). The authors concluded that according to their findings, a certain density of the monolayer as well as “kinetic stabilisation”, in the form of multivalent ligand binding, are required in order to achieve stability, with the effect of kinetic stabilisation being especially pronounced in liquid dispersions.

In other studies, the surface modification was targeted specifically in order to adjust the polarity of the nanoparticles, allowing their redispersion in a desired organic solvent or water. For example, TiO₂ aqueous sols were modified successfully with hydrophobic DTMS and hydrophilic APTMS to make the nanoparticles redispersible in solvents of different polarity, depending on the ratio of the used silanes (Iijima et al., 2009).

4.2 Instant stabilisation through surface modification

In some cases, the addition of ligands to an agglomerated particle system can prove sufficient to result in instant stabilisation. As an example, our earlier studies on the

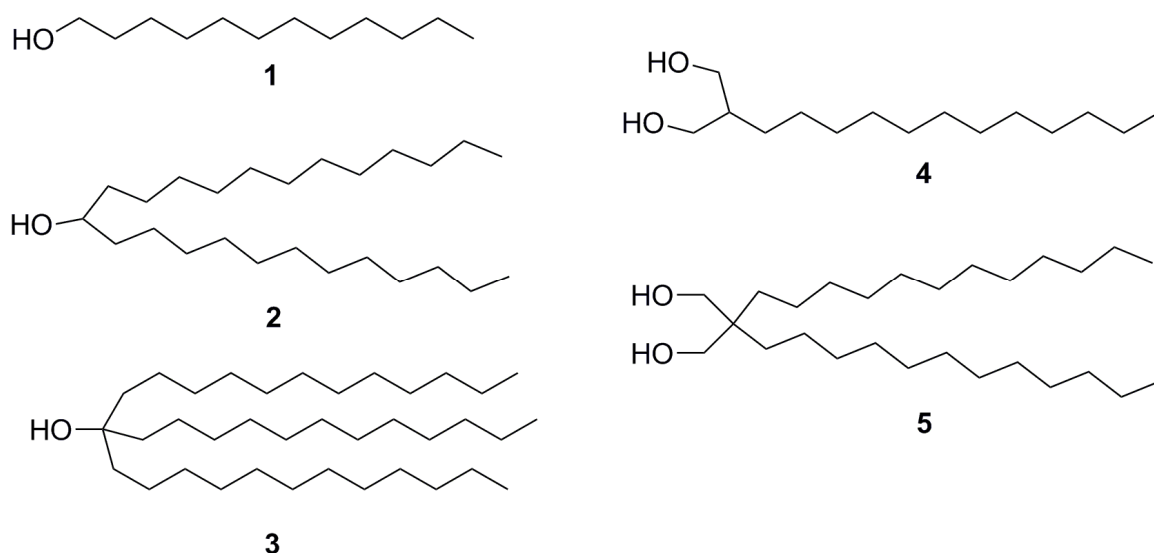


Fig. 7. Chemical structures of different ligands utilised for the modification of γ -Fe₂O₃ nanoparticles (after Boal et al., 2002).

stabilisation of ZrO₂ nanoparticles are presented (Garnweitner et al., 2007; Tsedev & Garnweitner, 2008). The nanoparticles were prepared in benzyl alcohol, which binds to the particle surface during the synthesis but is not capable of a full stabilisation. Hence, large agglomerates are obtained. After retrieval of the nanoparticles from the solvent by centrifugation and washing, solutions of fatty acid stabilisers were added, which resulted in instant stabilisation, visible as an immediate optical change of the mixture from turbid to transparent (Figure 8, left). TEM investigations of the nanoparticles after addition of the stabiliser show that the nanoparticles are fully stabilised, with no agglomeration occurring even during the drying process on the sample grid (Figure 8, right).

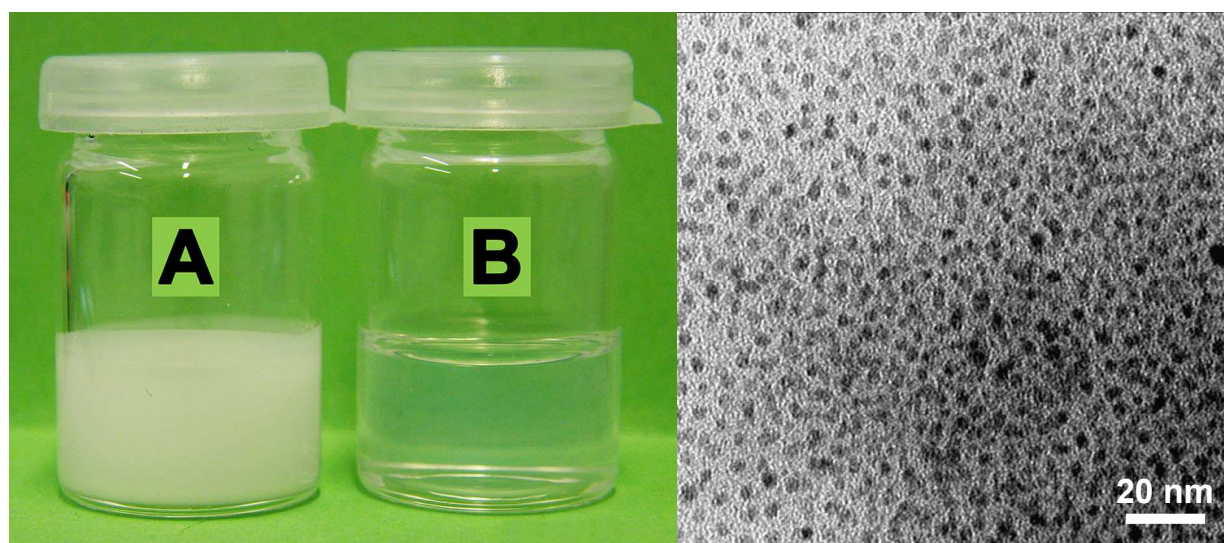


Fig. 8. Post-synthetic stabilisation of ZrO₂ nanoparticles by addition of fatty acids. Left: digital images of two samples before (A) and after (B) the stabilisation treatment; right: TEM image of oleic acid-stabilised nanoparticles.

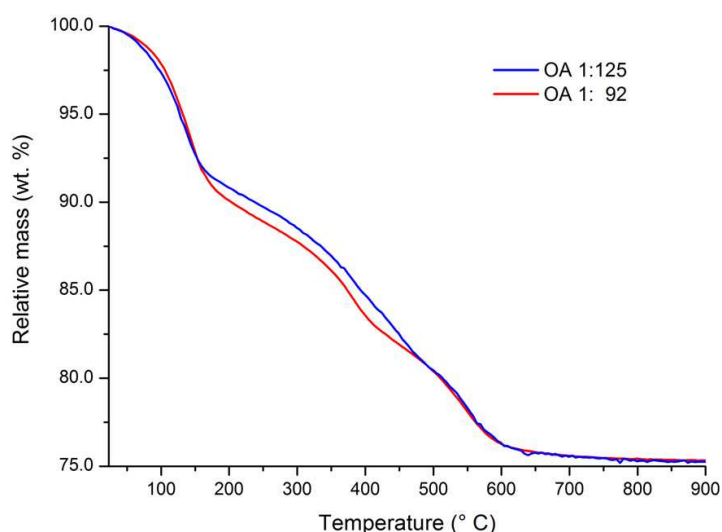


Fig. 9. Thermogravimetric analysis (TGA) of fatty acid-stabilised zirconia nanoparticles, with the stabiliser oleic acid (OA) added in different molar ratios.

In order to elucidate the binding of the fatty acid stabilisers in further detail, we performed thermogravimetric analysis of the nanoparticles before and after the stabilisation treatment. Even the as-prepared samples show a substantial amount of adsorbed organics, which can be attributed to benzyl alcohol coordinating to the particle surface during the synthesis (Niederberger et al., 2004). Figure 9 shows a comparison of two samples obtained when adding different concentrations of oleic acid (OA) as stabiliser, in a molar OA: ZrO_2 ratio of 1:125 (shown in blue), and 1:92 (shown in red). Both samples were fully stable against agglomeration. The thermograms show the same total mass loss of 24.7 wt. % at temperatures exceeding 800 °C for both samples, with however some differences in the decomposition behaviour at lower temperatures. Therefore, the total amount of organic and volatile species bound to the surface is equal, and does not rise even when increasing the amount of added stabiliser. By comparing the decomposition profile with samples measured before stabilisation and performing NMR spectroscopy (not shown), the observed differences could be attributed to a different ratio of adsorbed stabiliser to benzyl alcohol. Hence, when added above a certain concentration, the stabiliser does not increase the overall organics content of the nanoparticles, but replaces previously bound benzyl alcohol groups (Garnweitner et al., 2007).

In other investigations, however, the ligands were utilised rather to bind to a previously “bare” nanoparticle surface. This strategy is especially employed in cases of metal oxide nanoparticles synthesised by aqueous precipitation, where the resulting dispersions are charged-stabilised and highly sensitive to pH changes (Sehgal et al., 2005). Here, the binding of organic ligands can be utilised to considerably extend the range of pH stability, or achieve stability under completely different conditions. For example, the binding of poly(acrylic acid) (PAA) to CeO_2 nanoparticles was utilised to render the nanoparticles stable against agglomeration under alkaline conditions, which was attributed to an electrosteric mechanism (Sehgal et al., 2005). Figure 10 (a) shows a photograph of dispersions at different pH, proving the high stability in the alkaline regime. Additionally, DLS measurements performed by the group nicely illustrate the stabilisation process (Figure 10 (b)), with a

measurable steady decrease in particle size being the result of the stabilisation process upon pH increase (Sehgal et al., 2005). In a subsequent report, Qi et al. investigated the binding of phosphonated polyethylene glycol (PPEG) oligomers on ceria nanoparticles in a comprehensive binding study (Qi et al., 2008).

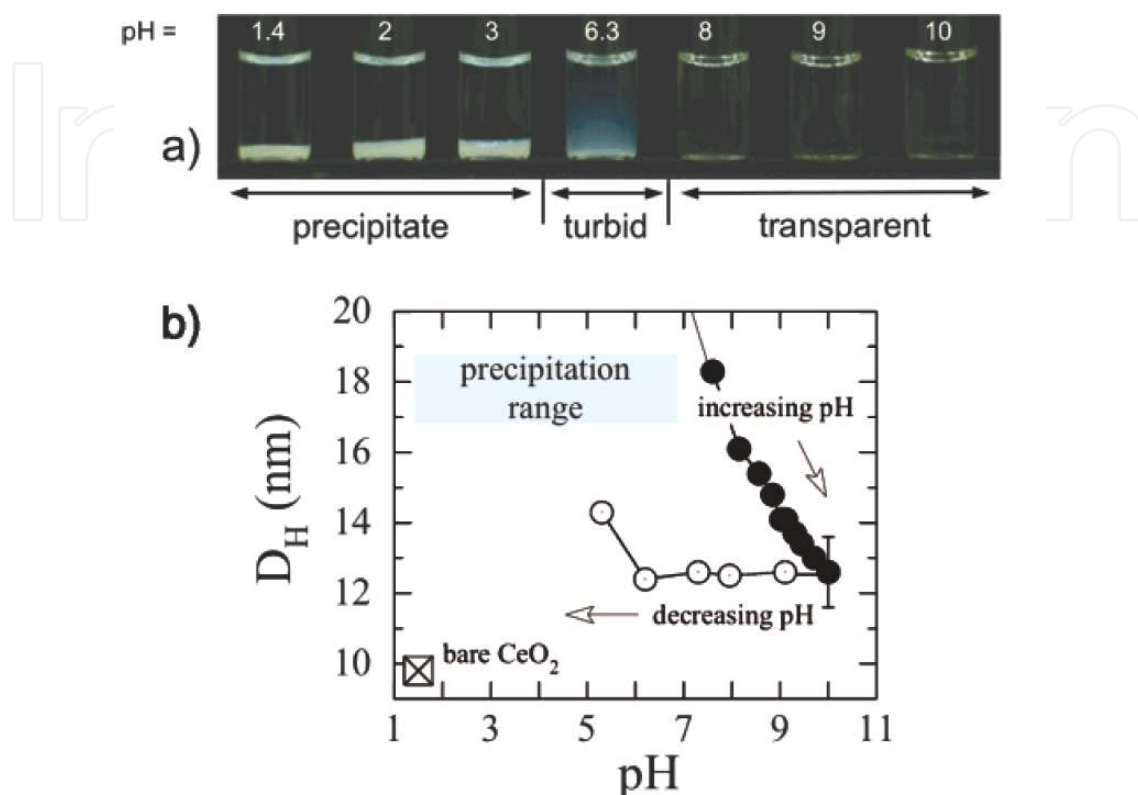


Fig. 10. Photographs of CeO₂-PAA solutions prepared at different pH, adjusted by NH₄OH (a); hydrodynamic particle diameters measured by DLS at different pH (b). Reprinted with permission from (Sehgal et al., 2005). Copyright 2005 American Chemical Society.

5. Conclusion

In this Chapter, a short review of the possibilities for the stabilisation of metal oxide nanoparticles using molecular organic stabilisers has been provided, showing select examples of the potentials of this strategy. In particular, the in-situ stabilisation technique has been compared to the post-synthetic stabilisation strategy. On the one hand, it was shown that the in-situ stabilisation strategy bears several drawbacks, as the particle properties, especially their crystallinity and morphology, may be adversely affected by the added ligands, that these problems however can be overcome by choice of the “right” ligand. The ideal in-situ stabiliser, therefore, needs to bind to the particle surface but not form too strong bonds, as this could interfere with the synthesis mechanism. For some metal oxides, such as TiO₂, first insights into the precise effect of different functional groups on the synthesis and stabilisation have been gained, and it can be expected that in the future, a toolbox will be available for different metal oxide systems, allowing the precise choice of an in-situ ligand for optimum effect. Then, the benefits of in-situ stabilisation can fully be exploited, such as the experimental simplicity and best stability.

Only in rare cases, a direct comparison of in-situ versus post-synthetic stabilisation has been performed, but these results clearly point to a higher efficiency of in-situ stabilisation approaches. For example, in the two-step stabilisation of magnetite nanoparticles, Theerdhala et al. achieved long-time stable dispersions only for the in-situ approach (Theerdhala et al., 2010). On the other hand, there are many cases where the initial reaction medium is not the perfect choice for further handling and storage of the nanoparticles, e.g. due to its toxicity or a too high or too low boiling point. In these cases, the post-synthetic stabilisation of nanoparticles will always be an attractive strategy, as the lack of stability of the nanoparticles allows for their simple and fast separation and recovery, and the presented examples clearly show that at least in some cases, a very simple and fast post-synthetic step is sufficient to achieve high stability of the nanoparticles, without any agglomeration even upon drying. Also in this case, it can be expected that within the next decade research on the chemical interaction of stabilisers and different metal oxide nanoparticle systems will lead to a much broader understanding than today, with general strategies available to enable the *a priori* choice of ligands at least for the most common metal oxides and reaction systems to achieve best stability with minimum addition of organics. Additionally, the increasing complexity of self-assembly tasks will also demand for structurally more complex ligands, which most likely will have to be introduced in post-synthetic steps due to their sensitivity to temperature and harsh chemical conditions. Hence, it appears clear that both the in-situ and post-synthetic approaches to the surface modification and stabilisation of nanoparticles will be applied in the future, with a more detailed knowledge being a fundamental prerequisite for the precise and rational application of experimental strategies to achieve optimum efficiency.

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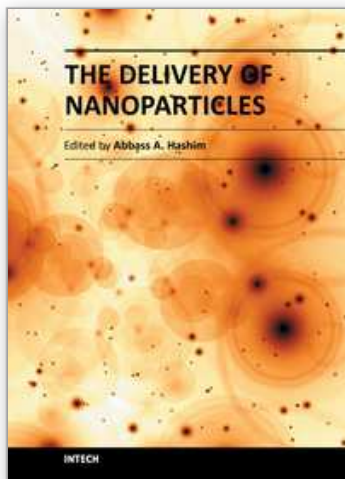
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The Delivery of Nanoparticles

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Nanoparticle is a general challenge for today's technology and the near future observations of science. Nanoparticles cover mostly all types of sciences and manufacturing technologies. The properties of this particle are flying over today scientific barriers and have passed the limitations of conventional sciences. This is the reason why nanoparticles have been evaluated for the use in many fields. InTech publisher and the contributing authors of this book in nanoparticles are all overconfident to invite all scientists to read this new book. The book's potential was held until it was approached by the art of exploring the most advanced research in the field of nano-scale particles, preparation techniques and the way of reaching their destination. 25 reputable chapters were framed in this book and there were alienated into four altered sections; Toxic Nanoparticles, Drug Nanoparticles, Biological Activities and Nano-Technology.

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